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PHASE TRANSFORMATIONS IN CHEMICALLY PRECIPITATED MIXTURES FOR ALUMOMAGNESIUM SPINEL

N. M. Bobkova,[1] E. V. Radion,[1] A. E. Sokolovskii,[1] and N. F. Popovskaya[1]

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The hydroxide precipitation method is used to produce initial materials for subsequent synthesis of alumomagnesium spinel. Using the IR spectroscopy and x-ray phase analysis methods, the processes of interaction between the materials obtained, phase transformations, and structure formation in alumospinel under thermal treatment are investigated. It is established that the spinel formation process passes via an intermediate phase, i.e., crystal hydrate $Mg_5Al_4O_{11} \cdot 15H_2O$, which in heat treatment transforms into aluminomagnesium spinel. With increasing temperature its structure is perfected and its quantity increases significantly. The formation of this phase ends at a temperature of 1300 – 1350°C.

Aluminomagnesium spinel $MgAl_2O_4$, due to its physicochemical properties, is currently one of the most promising construction materials. Its wide application is impeded by the difficulty of its production due to the very high temperatures of its synthesis from mechanical mixtures of MgO and Al_2O_3. The formation of spinel starts at the temperatures of 600 – 700 or 800 – 900°C and proceeds most intensely in the temperature interval of 1300 – 1500°C. However, the degree of transformation of $MgAl_2O_4$ at 1500°C is only 80%, at 1750°C — 86%, and at 1850°C — 88%. Furthermore, to produce articles from the spinel obtained, high temperatures of 1650 – 1750°C are again needed. Data on the complete transformation of magnesium spinel without adding various catalyst elements are virtually absent in the literature.

One of the directions for improving the technology is the use of fine chemical synthesis based on the precipitation method. This method is especially advisable for the synthesis of very high-melting compounds, including several minerals of the spinel type that have practical significance. The formation of spinel $MgAl_2O_4$ in samples produced by coprecipitation and subsequent calcination occurs at temperatures of 400 or 600 – 800°C [1, 2]. However, it is impossible to obtain spinel of stoichiometric composition (MgO in the free state is always present).

The authors of [3] studied the effect of various methods of producing solid phases in the $MgO - Al_2O_3 - H_2O$ system on their phase composition. It is demonstrated that the initial compounds in synthesis react with each other and form hydroxy compounds $MgAl_2(OH)_8$ (I) and $Mg_2Al(OH)_{7-x}(NO_3)_x$ (II), whose ratio depends on the ratio between the initial compounds and the method of their production. The maximum degree of interaction is attained in the coprecipitation of Mg^{2+} and Al^{3+} from salt solutions. Regardless of the method of producing Mg^{2+} and Al^{3+} hydroxides, compounds (I) and (II) containing sufficient quantities of nitrates dehydrate at a temperature of 450°C. Compound (II), in which the share of NO_3^- is insignificant, retains its structure up to a temperature of 850°C. In the samples precipitated by alkalis from salt solutions the formation of $MgAl_2O_4$ occurs at a temperature of 400°C, whereas when a mixture of Mg^{2+} and Al^{3+} hydroxides is calcined under the same conditions, the spinel phase is not registered even at a temperature of 800°C.

It is established that the phase composition of samples depends on the ratio of the components in precipitation. With a MgO molar content not more than 35%, the precipitate consists of $MgAl_2(OH)_8$ and excess aluminum hydroxide, and with a MgO content over 35% it consists of magnesium hydroxyaluminates $Mg_2Al(OH)_{7-x}(NO_3)_x$. The phase composition of samples after calcination also depends on the ratio of the components and their production method. A molar content of MgO over 50% produces spinel with increased lattice parameters and magnesium oxide. An increase in the temperature to 1000°C does not modify the phase composition of samples; only their structure becomes further perfected.

It is demonstrated in [4] that under homogeneous and heterogeneous precipitation of magnesium and aluminum hydroxides using ammonia it is difficult to ensure the production of spinel with a preset $MgO : Al_2O_3$ ratio, especially under industrial conditions.

Consequently, despite numerous studies dedicated to the production of magnesium spinel by the chemical precipitation method, there are certain contradictions in the descrip-

[1] Belarus State Technological University, Minsk, Belarus.

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tion of the processes of structure formation of spinel, the nature and chemical composition of the emerging compounds, and the phase composition of the precipitate. At the same time, the advisability of producing spinel by chemical precipitation is confirmed, since it becomes possible to decrease the synthesis temperature significantly.

The use of fine chemical synthesis for the production of the initial materials by the method of precipitation from solutions significantly changes the mechanism of structure formation and the sequence of phase transformations in the subsequent technological processes. These regularities are little studied for high-melting spinel-type compounds; therefore, it is necessary to perform additional studies in order to establish the scientific principles of using fine chemical synthesis in ceramic production.

The purpose of the present study is to investigate the interaction processes in mixtures of the synthesized initial materials, their phase transformations, and the structure formation of aluminospinels $MgO \cdot Al_2O_3$ under thermal treatment.

The initial solution for producing hydroxides was an aqueous solution of salts Mg(II) and Al(III), the precipitator being an alkali solution. The concentration of Mg^{2+} was determined by the comlexonometric method using eriochrome black T in a buffer ammonia medium [5] and the concentration of Al^{3+} was determined complexonometrically by inverse titration using zinc salt with xylenol orange in an acid medium [6]. Based on the analysis results, the solution with the ratio $Mg^{2+} : Al^{3+}$ equal to 1 : 2 was selected. The precipitation was carried out under the optimum conditions [7]. The pH was controlled using an I-160 ionometer. After aging, the precipitate was filtered and multiply washed with distilled water to remove adsorbed ions. The precipitate was dried to a constant weight in a SNOL drying cabinet at a temperature of 100 ± 5°C. After that they were calcined within a temperature interval of 170 – 1350°C with different durations of exposures.

Samples were sintered in a SNOL 6.7/1350 laboratory resistance furnace with a programmable numerical controller E5SK-T. The working space medium was air. The temperature rise was performed according to a program set by the software package: a uniform temperature rise at a rate of 5 K/min. The exposure at the maximum temperature was selected in accordance with the research target. The samples together with the furnace were cooled to room temperature. The temperature-time parameters of the heat treatment of samples are listed in Table 1.

After thermal treatment, the reaction products were analyzed by infrared spectroscopy (IRS) and x-ray phase analysis. The crystalline phases formed under heat treatment were identified by x-ray phase analysis (DRON-3 and DRON-4 with ionization detection of scattered rays, CuK_α-radiation, 1000 pulses/sec, Geiger meter used as the sensor). The diffraction patterns were decoded using the JCPDS diffraction database (USA). The IRS method (a Specord-75 IR spectrometer, range 400 – 4000 cm^{-1}, samples made by compressing powder into tablets with KBr at a ratio of 1 : 300) was used to study the phase transformations and to search for spectral manifestations of structural ordering in the crystalline state.

The diffraction patterns of the samples heat-treated at 170°C have peaks of $Mg_5Al_4O_{11} \cdot 15H_2O$. Consequently, Mg(II) and Al(III) enter into a reaction already in the course of precipitation. No peaks of individuals hydroxides or magnesium (II) and aluminum (III) oxides are registered (Fig. 1). At a temperature of 450°C weak reflections corresponding to the spinel of composition $MgO \cdot Al_2O_3$ (the peaks with interplanar distances d = 0.243, 0.201, and 0.143 nm) are observed on the diffraction curves. With increase in firing temperature up to 1300°C, the intensity of the peaks of spinel $MgO \cdot Al_2O_3$ increases.

The fluctuations in the intensity of the peak of 100% spinel depending on the heat treatment temperature is reflected in Fig. 2. A perceptible increase in intensity occurs within the temperature interval of 450 – 1300°C, whereas above 1300°C the intensity remains constant, which indicates the completion of the phase formation.

It is found that samples calcined at a temperature of 450°C already contain weak reflections with the interplanar

TABLE 1

Sample	Firing temperature, °C	Exposure duration, h	Phase composition according to x-ray phase analysis	Position of absorption band maxima on IR spectra, cm^{-1}
1	170	1 and 4	$Mg_5Al_4O_{11} \cdot 15H_2O$	557 – 669 (wide, blurred), 1024 (arm), 1385, 3467
2	320	1 and 4	Amorphous phase	451 (arm), 557 – 669 (wide, blurred), 1024, 1385, 3467
3	450	1 and 4	$MgAl_2O_4$ (crystalline)	451, 557, 669, 1024, 1385, 3467
4	600	1 and 4	The same	530, 700, 1024, 1385 (arm), 3467
5	700	2.5	〃	The same
6	800	1	〃	530, 700, 1024 (arm), 1385 (wide, weak), 3467
7	900	1	〃	The same
8	1000	1	〃	〃
9	1100	1	〃	530, 700, 1024 (wide, blurred), 1385 (wide, weak), 3467
10	1150	1	〃	The same
11	1200	1	〃	〃
12	1250	1	〃	〃

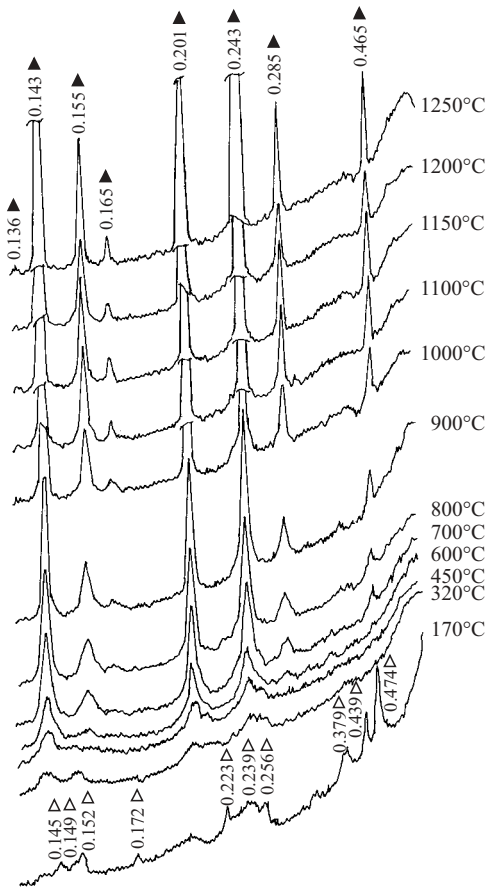

Fig. 1. X-ray patterns of the products of crystallization of coprecipitated mixtures depending on the heat treatment temperature: △) $Mg_5Al_4O_{11} \cdot 15H_2O$; ▲) $MgO \cdot Al_2O_3$.

distances typical of spinel $MgO \cdot Al_2O_3$, and in the temperature interval of 450 – 1350°C this is the only phase. An increase in the heat treatment temperature within the specified interval increases the quantity of spinel and perfects its crystal lattice.

Based on the studies performed and taking into account our data on the loss of water [7], the following scheme of phase transformations of the synthesized compound under heat treatment was revealed:

$$MgO \cdot Al_2O_3 \cdot nH_2O \xrightarrow{170^\circ C,\ -1.8H_2O}$$
$$Mg_5Al_4O_{11} \cdot 15H_2O \xrightarrow{320^\circ C,\ -1.2H_2O}$$
$$\text{amorphous phase} \xrightarrow{450^\circ C} \text{crystalline } MgAl_2O_4.$$

The IR spectra of samples obtained under different heat treatment conditions are shown in Fig 3. The position of the absorption bands (AB) in the spectra is indicated in Table 1.

The spectra of the samples fired at 170 and 320°C have blurred AB in the range of 500 – 1300 cm^{-1}, which points to the amorphousness of the samples. This agrees well with the x-ray phase analysis data. With increasing temperature the intensity of AB in the range of 1385 – 1024 cm^{-1} significantly decreases (nearly to their disappearance) and there are significant regular modifications in the form of the spectrum in the vibration range of the Me – O bond (500 – 700 cm^{-1}). At a temperature of 450°C two weakly resolved AB emerge from the wide blurred AB in the range of 557 – 669 cm^{-1} and their maxima shift to 530 and 700 cm^{-1}. With further increase in temperature, the resolution of these AB intensifies and the absorption intensity grows sharply. The clear narrowing of the AB indicates the formation of crystalline phases.

The AB in the range of 680 – 700 cm^{-1} may be attributed to the valence vibrations of octahedra $[AlO_6]$ in the bonded structures. Calculation of the coordination number of aluminum based on this AB band using the Dahil and Roy formula [8] confirms this assumption. The evident shift of

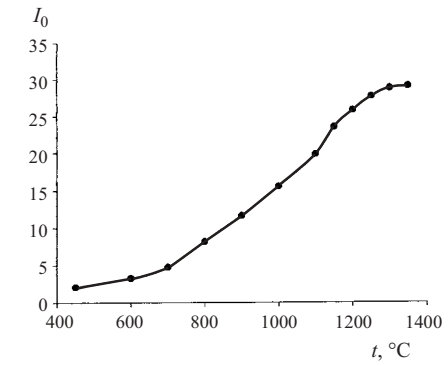

Fig. 2. Dependence of the intensity of the peak of 100% spinel with interplanar distance of 0.243 nm on heat treatment temperature.

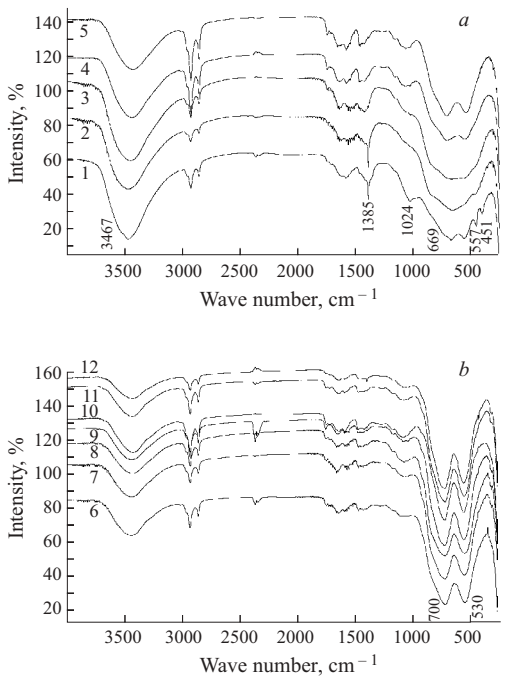

Fig. 3. IR spectra of synthesized samples 1 – 5 (*a*) and 6 – 12 (*b*). The numbers of samples correspond to those listed in Table 1.

AB 669 cm^{-1} to higher frequencies can be explained by the increased degree of bondedness of the octahedra.

The intense AB at 530 cm^{-1} can be attributed to the valence vibration of tetrahedra [MgO_4] in isolated groups, i.e., apparently separated by octahedra [AlO_6] [8].

Thus, the results of studies performed by the methods of IRS and x-ray phase analysis agree well and uniquely point to the formation of spinel via an intermediate phase, namely, crystal hydrate $Mg_5Al_4O_{11} \cdot 15H_2O$. When the precipitated compound is heat-treated, the only phase, i.e., alumino-magnesium spinel, emerges already at 450°C. With increasing firing temperature its structure is perfected and its quantity grows substantially. The formation of this phase is completed at a temperature of 1300 – 1350°C with an exposure of 1 h.

The development of theoretical principles of the synthesis of spinel from chemically precipitated compounds will make it possible to obtain this phase in a highly dispersed state with a high yield of the finished product and to significantly decrease the temperature of subsequent sintering of materials based on this product. This can solve the problem of producing high-density fire-resistant crystalline phases of the type of spinel $MgO \cdot Al_2O_3$ in a highly dispersed state.

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